

RI 8870



PLEASE DO NOT REMOVE FROM LIBRARY

Bureau of Mines Report of Investigations/1984

# **Lignite Recovery of Cobalt<sup>3+</sup> From an Ammoniacal Ammonium Sulfate Solution**

**By G. J. Slavens, Davis E. Traut, L. R. Penner,  
and Jack L. Henry**



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**Report of Investigations 8870**

# **Lignite Recovery of Cobalt<sup>3+</sup> From an Ammoniacal Ammonium Sulfate Solution**

**By G. J. Slavens, Davis E. Traut, L. R. Penner,  
and Jack L. Henry**



**UNITED STATES DEPARTMENT OF THE INTERIOR  
William P. Clark, Secretary**

**BUREAU OF MINES  
Robert C. Horton, Director**

Library of Congress Cataloging in Publication Data:

Lignite recovery of cobalt<sup>3+</sup> from an ammoniacal ammonium sulfate solution.

(Report of investigations ; 8870)

Bibliography: p. 11-12.

Supt. of Docs. no.: I 28.23:8870.

1. Cobalt--Metallurgy. 2. Lignite. 3. Ammonium sulphate.  
I. Slavens, G. J. (Gregory J.). II. Series: Report of investigations  
(United States. Bureau of Mines) ; 8870.

TN23.U43 [TN799.C6] 622s [669'.733] 83-600396

## CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Experimental procedures, equipment, and solutions.....	4
Results and discussion.....	5
Cobalt extraction.....	5
H <sub>2</sub> SO <sub>4</sub> pretreatment parameters.....	5
Cobalt extraction parameters.....	6
Cation extraction.....	7
Metal cations.....	7
Ammonia.....	7
Ammonium ion extraction.....	8
Cobaltic ammine extraction.....	8
H <sub>2</sub> SO <sub>4</sub> elution.....	9
Conclusions.....	11
References.....	11

## ILLUSTRATIONS

1. Laterite, reduction-roast, ammonia-leach method.....	3
2. Effect of pH on cobalt extraction by lignite.....	6
3. Effect of temperature on cobalt extraction by lignite.....	6
4. Effect of flow rate on cobalt extraction by lignite.....	7
5. Lignite column-exhaustion curve.....	7
6. Effect of H <sub>2</sub> SO <sub>4</sub> concentration on elution of cobalt from lignite.....	10
7. Effect of H <sub>2</sub> SO <sub>4</sub> concentration on cobalt concentration in the eluate.....	10
8. Effect of lignite bed height on elution of cobalt from lignite.....	10

## TABLES

1. Typical analyses of Ni-Cu raffinate.....	4
2. Effect of steam on NH <sub>4</sub> <sup>+</sup> :Co mol ratio in eluate.....	9

# UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

BV	bed volume	mg	milligram
BV/h	bed volume per hour	mg/L	milligram per liter
°C	degree Celsius	min	minute
cm	centimeter	mL	milliliter
g/L	gram per liter	pct	percent
h	hour	psig	pound per square inch, gage
lb	pound	wt pct	weight percent
<i>M</i>	molarity (mol per liter)		

# LIGNITE RECOVERY OF COBALT<sup>3+</sup> FROM AN AMMONIACAL AMMONIUM SULFATE SOLUTION

By G. J. Slavens,<sup>1</sup> Davis E. Traut,<sup>1</sup> L. R. Penner,<sup>2</sup> and Jack L. Henry<sup>3</sup>

---

## ABSTRACT

The Bureau of Mines has devised technology to recover cobalt, nickel, and byproduct copper from domestic lateritic material using an oxidative, ammoniacal ammonium sulfate leach. Nickel, cobalt, and copper were recovered by solvent extraction and electrowinning. To reduce the cost and complexity of cobalt recovery, an alternate method using lignite to extract Co<sup>3+</sup> was investigated as reported herein.

In the first 25 BV (bed volumes) of solution contacted with lignite, 97 wt pct of the Co<sup>3+</sup> was extracted in a downflow column at pH 9.3. After 85 BV, the lignite was loaded to 1.5 wt pct Co<sup>3+</sup> and further extraction was minimal. The lignite extracted cobaltic ammine complexes rather than cobalt ions and was nonselective as to other metal cations and ammonium ions.

Deleterious cations and 80 wt pct of the nonammine ammonium ions were removed prior to acid elution of the lignite. The removal of the amines prior to elution to produce an ammonium-ion-free Co<sup>3+</sup> eluate was only partially successful. Thus Co<sup>3+</sup> removal from ammoniacal solutions by lignite is technically difficult and economically unfeasible.

It was also determined that reduction of Co<sup>3+</sup> to Co<sup>2+</sup> occurred during the extraction-elution process.

---

<sup>1</sup>Chemical engineer.

<sup>2</sup>Research chemist.

<sup>3</sup>Supervisory research chemist.

Albany Research Center, Bureau of Mines, Albany, OR.

## INTRODUCTION

The Bureau of Mines has conducted research to recover metals from low-grade lateritic material found in Oregon and California and has devised a process to recover nickel, copper, and cobalt from these laterites (12-13, 18, 21-23).<sup>4</sup> Figure 1 is a diagram of the recovery process, which includes the following steps: (1) selective reduction roasting of the laterites with carbon monoxide, (2) leaching with a 2.8M  $\text{NH}_4\text{OH}$ , 2M  $(\text{NH}_4)_2\text{SO}_4$  solution, (3) selective solvent extraction of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  with LIX 64N,<sup>5</sup> leaving  $\text{Co}^{3+}$  in the raffinate, (4) extraction of metal impurities from the raffinate with IRC-718 resin, (5) reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  by contact with cobalt metal, (6) solvent extraction of  $\text{Co}^{2+}$  with LIX 51, and (7) acid stripping and electrowinning of the  $\text{Co}^{2+}$  to cobalt metal. The  $\text{Co}^{3+}$  reduction to  $\text{Co}^{2+}$  necessitates recycling one-third of the electrowon cobalt through steps 5, 6, and 7. A possible improvement to the process would be the direct extraction of  $\text{Co}^{3+}$ . Essentially, direct  $\text{Co}^{3+}$  extraction would reduce the processing costs by (1) eliminating the  $\text{Co}^{3+}$  reduction unit operation, (2) reducing equipment size, and (3) decreasing the cobalt inventory needed in the reduction step, which would also remove the source for cobalt concentration buildup in subsequent solutions.

A solvent extractant, neodecanoic acid, readily extracts  $\text{Co}^{3+}$  from this ammoniacal ammonium sulfate solution, but high solubility of this reagent in the aqueous solution makes it economically impractical (16).

Solid extractants such as ion-exchange resins have advantages over solvent extractants when large volumes of dilute solutions need to be contacted, as is the case in this process. These advantages include reduced solubility and a tendency

to increase the concentration of the desired ion in the eluate as compared to the concentration in the feed solution. Since the solution in this study contains less than 0.150 g/L  $\text{Co}^{3+}$ , solid extractants appear advantageous. However, no commercially available ion-exchange resins were reported in literature as successful extractants of  $\text{Co}^{3+}$  from ammoniacal ammonium sulfate solutions.

Lignite, a soft, brown coal, is another solid extractant used for removing metal values from solutions. Lignite has been used to extract cobalt of undisclosed valence from ammoniacal solutions (3),  $\text{Co}^{2+}$  from an ammoniacal sulfate solution (4), and  $\text{Co}^{2+}$  from ammoniacal carbonate solution (19). The most promising study used lignite to extract  $\text{Co}^{3+}$  from 0.4M ammoniacal ammonium carbonate solution at pH 9.5 (2). These studies indicate the usefulness of lignite as a cobalt extractant from basic ammoniacal solutions, although none directly address extraction from the ammoniacal ammonium sulfate solution that is produced in the proposed Bureau of Mines process. Therefore, the subject of this report is the evaluation of lignite extraction of  $\text{Co}^{3+}$  values from the ammoniacal ammonium sulfate leach solution.

Potential problems have also been defined in the extraction of  $\text{Co}^{3+}$  from ammoniacal solutions. The nonselective extractive properties of lignite are well documented (1, 3-4, 15, 24) and pose a problem for the selective extraction of  $\text{Co}^{3+}$ . Additionally, cobaltic ammine<sup>6</sup> complexes are present in ammoniacal ammonium solutions (8) and are often loaded intact by extractants (7, 16). Elution of cobaltic amines from the extractant could result in electrolyte contamination by ammonium ions (7, 16).

<sup>4</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

<sup>5</sup>Reference to specific products does not imply endorsement by the Bureau of Mines.

<sup>6</sup>In the following discussions, the term "ammine" designates the ammonia coordinated with  $\text{Co}^{3+}$ , while ammonia, not associated with a cobaltic ammine, is referred to as ammonium ion. The word "ammonia" is used as a general term or to refer to ammonium ions and amines together.

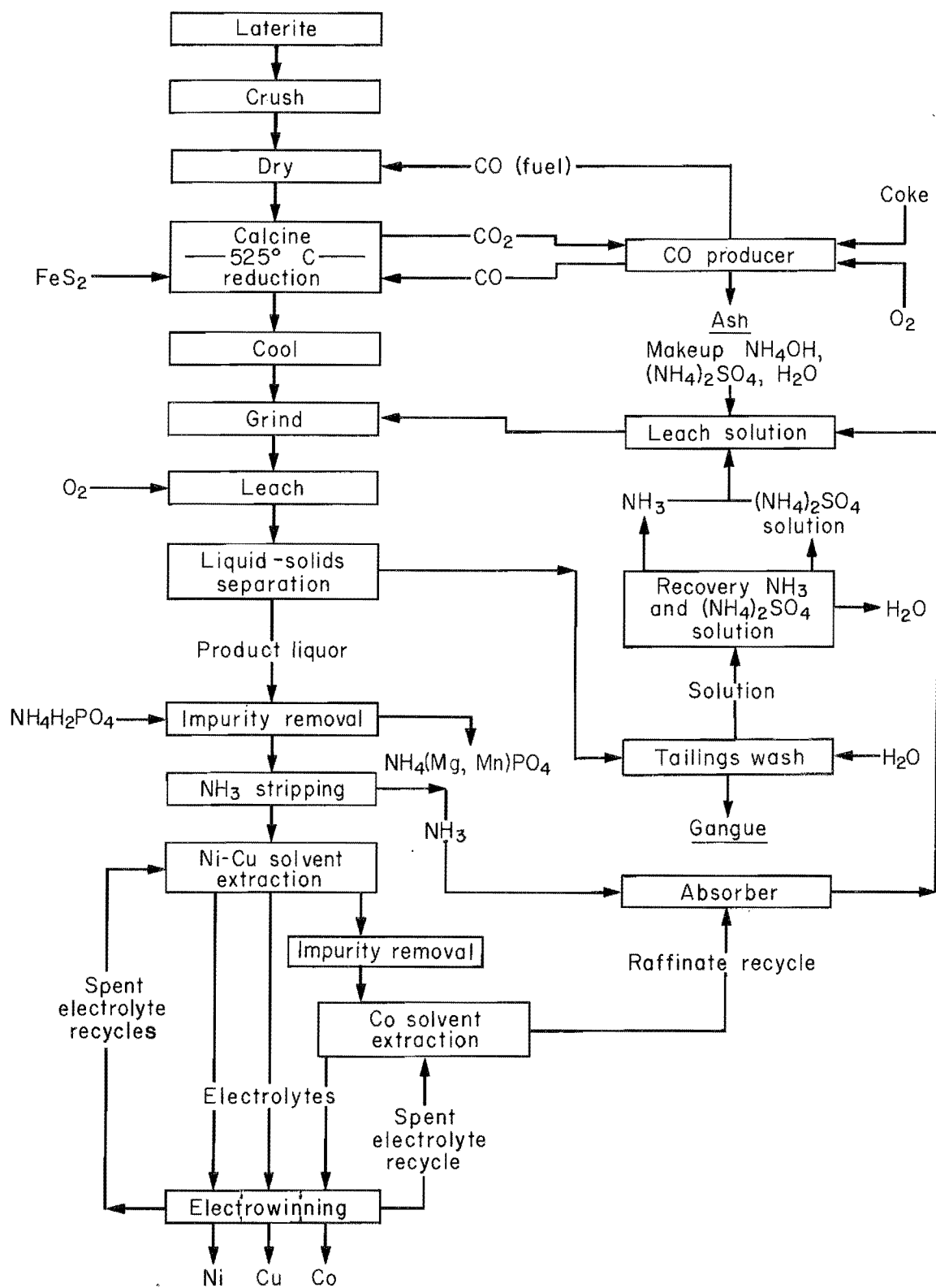


FIGURE 1. - Laterite, reduction-roast, ammonia-leach method.



Efficient extraction of  $\text{Co}^{3+}$  is only the first step in a successful process. The cobalt should be recovered from the lignite in a pure, concentrated solution that allows the recovery of cobalt metal by an economical process such as electro-winning. Elution of cobalt from the lignite with inorganic acid has been suggested (2, 4, 19), but very little has been published on elution results.

#### EXPERIMENTAL PROCEDURES, EQUIPMENT, AND SOLUTIONS

Lignite extraction and elution tests were performed in batches and columns. Lignite was measured as wet settled volume (WSV), which is the volume of lignite in a water medium shaken on a vortex mixer until the lignite volume no longer changes. In batch tests, the desired wet settled volume of lignite was contacted with solution and shaken in an orbital shaker for the desired time at the desired temperature. The solid and liquid were separated by filtration, and the liquid phase was analyzed for cobalt by atomic absorption spectroscopy.

Column tests were conducted with a prescribed volume of lignite (WSV) in a water-jacketed glass column. The lignite bed measured 0.9 cm in diameter and 14 cm in height except when bed height effects were examined. Preheated leach liquor or eluant acid was pumped through the preheated and continuously heated lignite bed, which permitted tests at different temperatures. The collected effluent was then analyzed. Cobalt concentration in the solution before and after extraction was used to determine cobalt loading on the lignite. Solution nitrogen analysis by the Kjeldahl method was used to measure ammonium ion levels.

Actual laterite leach liquor was used for all extraction tests. Nickel and copper had been removed previously by LIX 64N extraction. Trace cations were then removed by contact with IRC 718 ion exchange resin (a chelating, cationic resin for transition metals). This processed solution, referred to as Ni-Cu raffinate, contained about 2M  $(\text{NH}_4)_2\text{SO}_4$  and 5 g/L free  $\text{NH}_3$ , with a pH range of 9.0 to 9.5.

This report describes and quantifies, but does not optimize, the extraction of  $\text{Co}^{3+}$  from an ammoniacal ammonium sulfate solution by lignite. Also discussed is the nonselectivity of lignite as an extractant, particularly regarding coextracted ammonium ions and complexed amines. Finally, cobalt elution from lignite is discussed to quantify the ammine problem.

Typical analyses are given in table 1. Since lignite is a nonselective extractant, IRC 718 or a similar divalent ion-exchange resin was essential for removing most divalent cations, leaving a relatively pure  $\text{Co}^{3+}$  solution.

TABLE 1. - Typical analyses of Ni-Cu raffinate

Ions	Ni-Cu raffinate analysis, g/L	
	Before IRC 718	After IRC 718
Ca.....	0.01	0.003
Co.....	.14	.14
Cu.....	.0006	.0006
Fe.....	.001	.001
Mg.....	.01	.004
Mn.....	.005	.0003
Na.....	.05	.05
$\text{NH}_3$ .....	5.0	5.0
Ni.....	.05	.001
$\text{SO}_4$ .....	197.0	197.0
Zn.....	.04	.0007

$\text{Co}^{3+}$  in the ammoniacal feed solution<sup>7</sup> existed as an ammine complex; therefore, it was important to analyze the ammine-cobalt ratio. Using cobalt compounds dissolved in 2M ammoniacal ammonium sulfate solution as standards, a high-pressure liquid chromatograph (HPLC) was used to identify the cobaltic ammine complexes in the Ni-Cu raffinate. It was determined that 85 pct of the  $\text{Co}^{3+}$  was cobaltic hexammine  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , with the remainder being cobaltic pentammine  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ . Very small amounts of cobaltic tetrammine  $[\text{Co}(\text{NH}_3)_4\text{SO}_4]^+$  were also identified in the solution after

<sup>7</sup>For simplicity,  $\text{Co}^{3+}$  is used to refer to trivalent cobalt in the feed solution.

lignite contact. The identification technique used for this sulfate solution closely followed one developed for a carbonate system (8).

The lignite used for extraction studies was obtained from the Beulah Mine, Beulah, ND. It was ground, sized, and stored wet until used. Sulfuric acid pretreatment of the lignite to enhance extraction (2-3, 9, 20) was accomplished by shaking  $\frac{4}{1}$  BV (bed volumes) (1 BV is

equal to the WSV of lignite used) of 20 wt pct  $\text{H}_2\text{SO}_4$  with 1 BV wet lignite for 30 min at 55° C. This was followed by thorough water washing and wet storage before contact with Ni-Cu raffinate for extraction.

The cobalt valence state in the eluate was important for electrolytic recovery. An EDTA-standardized zinc titration procedure (10) was conducted to measure any  $\text{Co}^{2+}$  in the solution.

## RESULTS AND DISCUSSION

To be effective and economically competitive, an extractant needs favorable characteristics for loading and eluting the desired metal values. For extraction, ideal characteristics include high affinity leading to desirable kinetics, high selectivity, and conditions such that these two characteristics can be attained economically (e.g., low temperature, large extractant particle size, and little solution adjustment). Successful elution requires the desired ion to be more concentrated in the eluate than in the feed solution, an eluate from which metal can be recovered with ease, and conditions such that these characteristics can be attained economically.

With these characteristics in mind, lignite was studied as an extractant for the  $\text{Co}^{3+}$  present in the Ni-Cu raffinate. First, the effective extraction parameters were determined. Next, the extent and effects of simultaneous ammonium ion and ammine complex ion extraction were determined. Finally, elution parameters were studied. The extraction parameters were not optimized but were studied to establish trends that would ensure adequate  $\text{Co}^{3+}$  extraction by lignite. Likewise, elution parameters were not optimized but were studied to evaluate the effects of eluted ammonium ions and ammines on the resulting solution.

### COBALT EXTRACTION

A series of experiments to enhance the extraction of  $\text{Co}^{3+}$  by lignite was conducted. The effectiveness of lignite was measured with respect to weight

percent available  $\text{Co}^{3+}$  extracted and total amount of  $\text{Co}^{3+}$  loaded per unit weight of lignite. The following parameters were evaluated:

1. Acid pretreatment of lignite prior to first extraction contact.
2. Solution pH.
3. Extraction contact temperature.
4. Solution flow rate.
5. Lignite particle size.

#### $\text{H}_2\text{SO}_4$ Pretreatment Parameters

Sulfuric acid pretreatment of lignite prior to the first extraction contact enhances  $\text{Co}^{3+}$  extraction, although the mechanism for this is not known (9, 20). Batch tests on acid pretreatment of lignite were conducted to study the acid concentration strength and quantity, and the acid-lignite contact temperature and duration. Acid concentrations greater than 20 wt pct  $\text{H}_2\text{SO}_4$  did not improve  $\text{Co}^{3+}$  extraction, while concentrations less than 20 wt pct  $\text{H}_2\text{SO}_4$  reduced  $\text{Co}^{3+}$  extraction. Acid quantities ranging from 1 to 8 BV, contact temperatures of 24° to 65° C, and contact times of 5 to 60 min also did not further improve  $\text{Co}^{3+}$  extraction. However, pretreatment of lignite with 20 wt pct and 4 BV  $\text{H}_2\text{SO}_4$  acid at 55° C and 30 min contact increased  $\text{Co}^{3+}$  extraction by 11 wt pct, as compared to untreated lignite. Therefore, acid-pretreated lignite at these favorable conditions was used for all subsequent tests.

### Cobalt Extraction Parameters

In the high-pH range excess ammonium ions compete with  $\text{Co}^{3+}$  for extraction by lignite. In the low-pH range  $\text{H}_3\text{O}^+$  strips  $\text{Co}^{3+}$  from the lignite. To adjust the pH of Ni-Cu raffinate for batch tests, the solution was either sparged with anhydrous ammonia or 2.5M sulfuric acid was added. Figure 2 clearly shows maximum  $\text{Co}^{3+}$  extraction between an initial solution pH of 9.2 and 9.5 (equilibrium pH 9.1 and 9.4). Since the Ni-Cu raffinate pH ranged from 9.0 to 9.5, no pH adjustment was necessary.

Increasing the extraction contact temperature should enhance  $\text{Co}^{3+}$  extraction by improving kinetics, but higher temperatures are more expensive and cause greater ammonia loss from solution. Extraction results at four temperatures (fig. 3) show a reduction in  $\text{Co}^{3+}$  extraction with lower temperature. Very little difference in extraction was seen between 40° and 55° C, and no difference was seen between 55° and 70° C. Room temperature extraction (22° C) was much poorer than

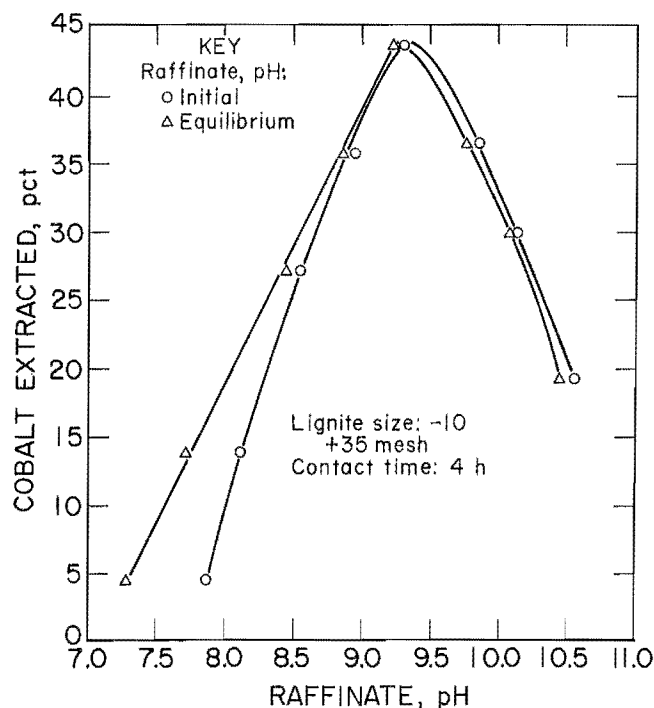


FIGURE 2. - Effect of pH on cobalt extraction by lignite. Batch contact with a lignite-to-available- $\text{Co}^{3+}$  weight ratio of 100:1.

extractions at the higher temperatures. These results indicate that  $\text{Co}^{3+}$  extraction is improved by raising the temperature to above 40° C, but above that temperature no significant improvement was seen. All subsequent contacts were made at 55° C to ensure adequate  $\text{Co}^{3+}$  extraction.

The flow rate through a column determines retention time, which affects extraction. The highest possible flow rate without loss in extraction efficiency is desirable. At 55° C,  $\text{Co}^{3+}$  extraction decreased at flow rates higher than 3.0 BV/h after 20 BV had been contacted (fig. 4). Therefore, a 3.0-BV/h flow rate was used for all subsequent experiments.

Lignite particle size was the last extraction parameter investigated. Smaller lignite particle size increases surface area and thus improves kinetics. However, a small particle size also increases the pressure drop across the bed, compounds handling difficulties, and

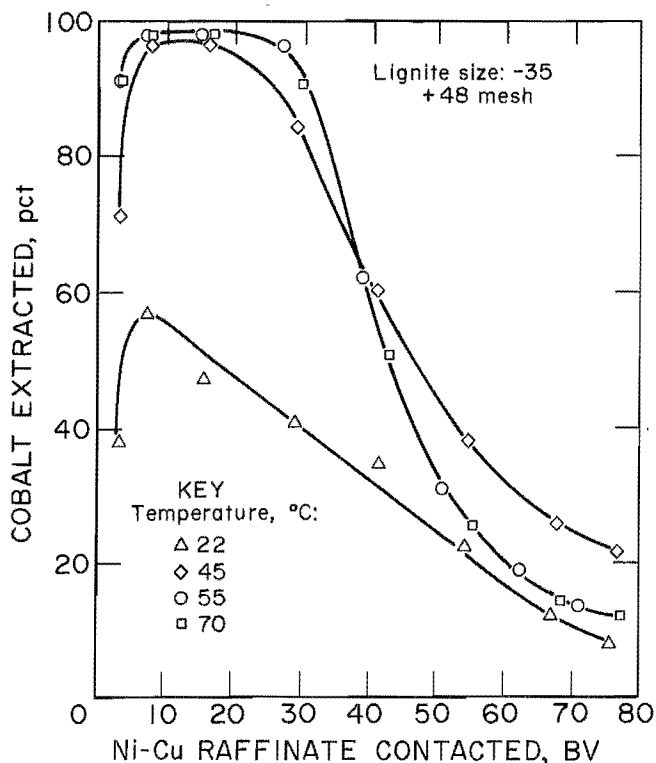


FIGURE 3. - Effect of temperature on cobalt extraction by lignite. Column contact using 9.3 pH Ni-Cu raffinate.

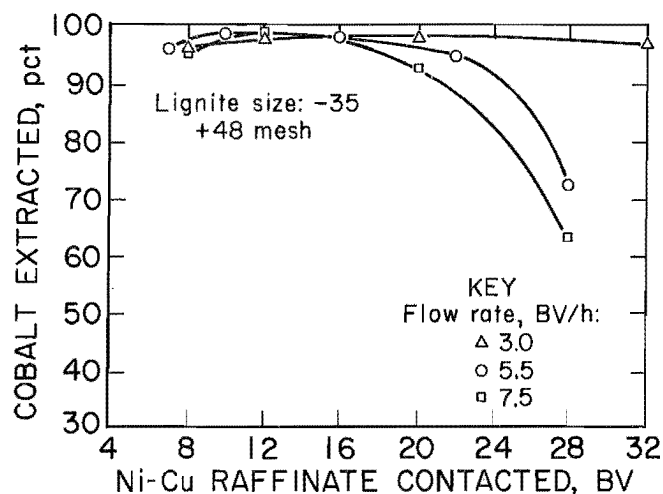


FIGURE 4. - Effect of flow rate on cobalt extraction by lignite. Column contact using 9.3 pH Ni-Cu raffinate.

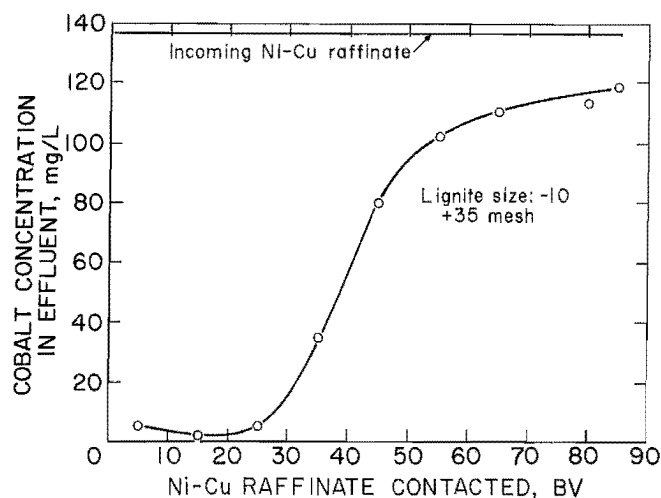


FIGURE 5. - Lignite column-exhaustion curve. Column contact using 9.3 pH Ni-Cu raffinate.

increases particle losses. Batch contacts were conducted at 55° C with a 100:1 weight ratio of H<sub>2</sub>SO<sub>4</sub>-pretreated lignite to cobalt. At a minus 10- plus 35-Tyler mesh lignite size, 54 pct of the Co<sup>3+</sup> was extracted; using smaller lignite (minus 35 plus 48) 70 pct was extracted. A minus 35- plus 48-mesh fraction was employed for all cation coextraction and elution tests, although two particle sizes were used to study the preceding Co<sup>3+</sup> extraction trends as indicated by the varying Co<sup>3+</sup> extraction amounts in figures 2-5.

To summarize the parameters of Co<sup>3+</sup> extraction by lignite, it must first be remembered that these parameters have not been optimized. Only trends have been studied to increase cobalt extraction for use in selectivity experiments. In addition, Co<sup>3+</sup> extraction could be enhanced by using larger columns with deeper lignite beds (5-6), thus improving the column-exhaustion curve (fig. 5), which shows as high as 97 wt pct Co<sup>3+</sup> extraction up to 25 BV, which with additional data calculates to 1.5 wt pct loading after 85 BV. The weight percent Co<sup>3+</sup> extracted and the total Co<sup>3+</sup> loaded must be balanced by economic considerations.

#### CATION EXTRACTION

Lignite selectivity was examined to determine the extent of contamination in the recovery of cobalt. The three areas of concern with respect to selectivity in using lignite to extract Co<sup>3+</sup> from Ni-Cu raffinate were (1) extracted metal cations other than Co<sup>3+</sup>, (2) extracted ammonium ions, and (3) extracted amines. All three were extracted from the Ni-Cu raffinate and became problems when eluted. To avoid these problems, the contaminants must be removed from the Ni-Cu raffinate, the lignite, or the eluate.

#### Metal Cations

Since lignite extracts cations almost nonpreferentially, metal cations other than Co<sup>3+</sup> should be reduced to an acceptable level such that the cobalt metal product is not contaminated. Ideally, these metal cations should be removed before solution contact with lignite, since they would occupy sites on the lignite needed for Co<sup>3+</sup> extraction. Table 1 shows the results of using IRC 718 ion-exchange resin to remove many of the undesired cations and to reduce their concentration to an acceptable level before lignite contact.

#### Ammonia

In the Co<sup>3+</sup> extraction process for an ammoniacal system followed by an acidelectrowinning step, it is vitally

important to avoid transfer of ammonia from feed solution to electrolyte (16). Any ammonia remaining on the lignite that has not been removed prior to elution will transfer to the eluate and cause two serious problems: (1) Ammonia will be neutralized by the acid, resulting in acid makeup costs, and (2) the neutralization product, the ammonium-cobalt double salt  $[(\text{NH}_4)_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}]$ , will build up until it ultimately crystallizes and fouls the electrolyte (12).

#### Ammonium Ion Extraction

At the normal pH (9.0 to 9.5) of Ni-Cu raffinate, extraction of ammonium ions with  $\text{Co}^{3+}$  was unavoidable. Typical analyses indicated 15 mol of ammonium ions were extracted by lignite for every mol of  $\text{Co}^{3+}$ , not including the amines. Batch washing tests were conducted with three successive water washes at 55° C for 8 h at a 25:1 distilled-water-to-lignite volume ratio. The extracted ammonium ions were reduced to about 3 mol for each mol of  $\text{Co}^{3+}$ .

Although the water washes did not remove all of the ammonium ions, the level was lower than the residual amines of the cobaltic complexes, which were found to be more difficult to remove. Therefore, the remaining experiments focused on amines removal.

#### Cobaltic Ammine Extraction

Lignite, like many other extractants, extracts the very stable, cobaltic ammine complex (7) rather than just  $\text{Co}^{3+}$ . Therefore, experiments were directed toward removing the amines from the cobaltic complex loaded on the lignite.

It would be advantageous to know the number of amines in the extracted cobaltic complex, but no practical method was found for identifying this complex while it was on the lignite. However, cobaltic hexammine was assumed to be the ammine species predominant on the lignite for two reasons: (1) Cobaltic hexammine is very stable at the solution pH (7-8) and (2) HPLC studies showed that cobaltic

hexammine was the predominant ammine species removed from Ni-Cu raffinate by lignite. The amines proved to be far more tenacious than the ammonium ions and therefore more difficult to separate.

A series of tests was conducted to remove the amines present on the lignite from the  $\text{Co}^{3+}$  complex. These tests concentrated on pH-controlled washing and steam stripping since they were the least expensive of the alternatives. The effectiveness of a test was measured by the resulting  $\text{NH}_4^+:\text{Co}$  mol ratio found in the eluate. This mol ratio should be kept as low as possible to prevent eluate contamination. If all of the extracted ammonium ions were removed prior to acid elution and only cobaltic hexammine was loaded, 6 mol of ammonium ions would be found for every mol of cobalt eluted. Therefore, if less than 6 mol of ammonium ions to every mol of  $\text{Co}^{3+}$  is found, this represents a removal of ammonia from the ammine complex.

A number of loaded lignite samples were contacted batchwise using varying concentrations of dilute  $\text{H}_2\text{SO}_4$  as the pH-controlled wash. The method met with only partial success. The best  $\text{NH}_4^+:\text{Co}$  mol ratio achieved was 2.7, following a dilute acid wash at equilibrium pH 4 using 25 times as much wash volume as lignite. At lower pH values the amines removal was effective but at the cost of also removing cobalt. At higher pH values the amines removal was ineffective.

Since a pH-controlled wash did not remove all amines, steam stripping for amines removal was tested. Preheated, loaded lignite samples were steam-stripped with either 12 or 50 psig (118° C and 148° C, respectively) steam for various lengths of time. Then the steam-stripped lignite was eluted with acid to remove cobalt and any remaining amines. Finally, the steam condensate and the elution acid were analyzed for ammonium ions and cobalt (table 2). Small amounts (low condensate volumes) of either 12- or 50-psig steam produced very similar  $\text{NH}_4^+:\text{Co}$  mol ratios. However,  $\text{NH}_4^+:\text{Co}$  mol ratios below 3.0 were not achieved.

Large amounts of steam yielded lower  $\text{NH}_4^+:\text{Co}$  mol ratios, although neutralization acid was still required.

TABLE 2. - Effect of steam on  $\text{NH}_4^+:\text{Co}$  mol ratio in eluate

Steam pressure, psig	Condensate volume, mL	$\text{NH}_4^+:\text{Co}$ ratio
118° C:		
12.....	28	5.0
12.....	120	4.3
148° C:		
50.....	27	5.1
50.....	113	3.1
50.....	1,474	.6

In summary, water washing, pH-controlled washing, and steam stripping proved ineffective in removing ammonia and amines from lignite. Ammonium ion would still continue to build up in the electrolyte faster than a reasonably sized bleed stream could remove it. Therefore, lignite appears to be an unacceptable extractant for  $\text{Co}^{3+}$  from this solution because of ammonium ion contamination.

The economics of ammonia removal are also not presently acceptable. Total acid neutralization to remove 3 mol of extracted ammonium ions and 6 mol of amines per mol of Co required 4.5 mol  $\text{H}_2\text{SO}_4$  costing \$0.30/lb of Co produced (17). This acid neutralization produces an increased ion concentration in the eluate, which would eventually crystallize out the ammonium-cobalt double salt. Since a reasonably sized bleed stream could not control this buildup, crystal removal from the eluate would be required.

An alternative to complete acid neutralization is partial removal of extracted ammonium ions and cobaltic amines by steam stripping, requiring lower acid usage. A typical low steam usage experiment used 0.060 lb of steam costing \$3/lb Co produced (17). This lowered the  $\text{NH}_4^+:\text{Co}$  mol ratio to 5, requiring an additional 2.5 mol  $\text{H}_2\text{SO}_4$ , costing \$0.17/lb Co produced, for neutralization (17). Increased steam volumes reduced the

$\text{NH}_4^+:\text{Co}$  mol ratio and acid usage but greatly increased the cost for steam stripping. These costs presently favor acid neutralization over steam stripping, unless waste steam is available, but increased acid neutralization increases the crystal buildup problem.

Excluding ammonia removal and electrowinning, the capital and operating costs of the proposed cobalt reduction-solvent extraction process and the lignite process are projected to be nearly equal (17). Since the former process requires only an estimated additional \$0.084/lb Co recovered for electrowinning (17), the lignite process must remove ammonia and electrowin an equal amount of cobalt for less cost. Clearly, the lignite process cannot do this and is economically a less desirable process than the presently proposed one.

This cobaltic ammine extraction and subsequent amines separation is a fundamental problem which would need to be solved for all cobaltic ammine systems.

#### $\text{H}_2\text{SO}_4$ ELUTION

To quantify the ammonia effect on the process, elution studies were also carried out. Cobalt elution parameters were studied to maximize the cobalt concentration and minimize the ammonium ion effects in the eluate, although no attempt was made to optimize the parameters. Results were evaluated based on two criteria: (1) the cobalt concentration in the eluate and (2) the volume of eluate gathered before the concentrated cobalt solution appeared. Elution parameters evaluated include (1) temperature, (2) eluant flow rate, (3) eluant concentration, and (4) lignite bed height.

Temperatures in the range of 20° C to 70° C and eluant flow rates between 1 and 7 BV/h had negligible effects on cobalt elution. Therefore, a temperature of 55° C and a 2-BV/h flow rate were used in all subsequent tests to assure adequate elution.

The acid concentration in the eluant and in the resulting eluate is an important consideration because it affects both cobalt concentration and electro-winning efficiency. Raising the  $H_2SO_4$  eluate concentration lowers electro-winning current efficiency because increasing amounts of hydrogen are evolved (11, 14). However, ammonium sulfate, either formed as a neutralization product or added, acts as a pH buffer and improves conductivity (14).

The results of using 2, 5, and 10 wt pct  $H_2SO_4$  as the eluant are plotted in figure 6. Increasing the acid concentration resulted in using fewer bed volumes of solution before cobalt is eluted. The additional solution required at lower acid concentration would either dilute the eluate or create a greater total volume that must be recycled or treated and discarded. Furthermore, figure 7 shows that the eluate cobalt concentration is higher using 10 wt pct  $H_2SO_4$  than at lower acid concentrations. Therefore, 10 wt pct  $H_2SO_4$  was used for all subsequent elution tests.

As the lignite bed height is increased, the countercurrent effect in the bed also increases, which improves lignite

extraction efficiency (5-6). This advantage created by the increased height, which is offset by greater capital cost and pressure drop, may also be true for elution. Bed height results (fig. 8) show that the cobalt concentration in the eluate increased with height. This occurs because an equal eluant volume contacts more loaded lignite, thus eluting more cobalt.

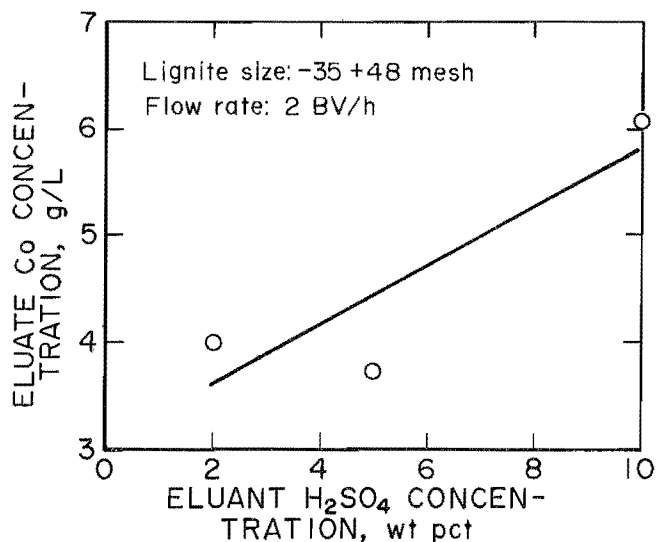


FIGURE 7. - Effect of  $H_2SO_4$  concentration on cobalt concentration in the eluate. Column contact.

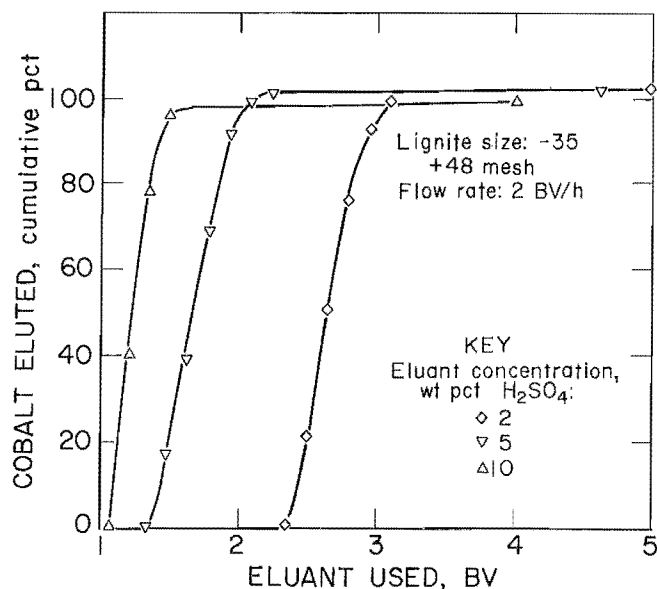


FIGURE 6. - Effect of  $H_2SO_4$  concentration on elution of cobalt from lignite. Column contact.

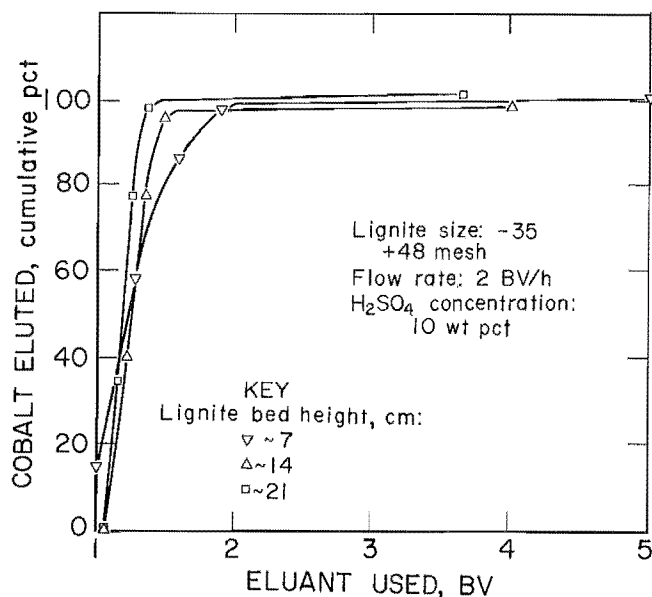


FIGURE 8. - Effect of lignite bed height on elution of cobalt from lignite. Column contact.

While studying methods to remove ammonia from the loaded lignite and the subsequent acid elution, two phenomena were observed. First, elution, following steam stripping, required a larger eluant volume, thereby decreasing the cobalt concentration in the eluate. As a result, steam stripping to remove ammonia from lignite was costly not only in steam usage but also in reduced elution efficiency.

### CONCLUSIONS

The recovery of  $\text{Co}^{3+}$  from an ammoniacal ammonium sulfate leach liquor using lignite as the extractant was studied. In column tests, lignite extracted 97 wt pct  $\text{Co}^{3+}$  in the first 25 BV of solution contacted. After 85 BV the loaded lignite contained 1.5 wt pct  $\text{Co}^{3+}$ .

The  $\text{Co}^{3+}$  was extracted as a cobaltic ammine complex. No economically acceptable method for selectively separating the amines from the cobaltic complex while leaving the cobalt on the lignite was found. Both steam stripping and a pH-controlled wash removed some of the amines but presented cost, crystallization, and/or dilution problems. The stability of the cobaltic ammine complex is such that the problem would be encountered for extraction of  $\text{Co}^{3+}$  from any ammoniacal solution.

The nonselective extractive nature of lignite resulted in the simultaneous

The second phenomenon involved the reduction of  $\text{Co}^{3+}$  loaded on the lignite to  $\text{Co}^{2+}$ . Elution with acid removed 90 to 100 wt pct of the cobalt, all of which was analyzed as  $\text{Co}^{2+}$ . Since the valence state of the cobalt on the lignite could not be identified, the reduction mechanism, whether during extraction or elution, could not be proposed.

extraction of divalent metal cations and ammonium ions. The divalent metal cations were sufficiently removed from the Ni-Cu raffinate by IRC 718 ion-exchange resin. Eighty percent of the ammonium ions were removed from the loaded lignite by successive water washes. Sulfuric acid effectively eluted the cobalt from lignite, but any remaining ammonium ions and amines also were removed, thus contaminating the eluate. Separation of these residual ammonia groups from the cobalt proved to be a technical problem that was not satisfactorily solved. Furthermore, all attempts to remove these groups were more expensive than the previously proposed method to reduce  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  with cobalt metal followed by solvent extraction prior to electrowinning.

Also noted with the use of lignite for  $\text{Co}^{3+}$  extraction followed by acid elution was the reduction to  $\text{Co}^{2+}$  during the extraction-elution process.

### REFERENCES

1. Altekar, V. A., M. J. Shahani, and A. K. Saha. Adsorption of Nickel by Lignite. *Fuel*, v. 53, Jan. 1974, pp. 29-31.
2. Bradbury, J. A., and R. T. Um (assigned to UOP Inc., Des Plaines, IL). Recovery of Cobalt Values. U.S. Pat. 4,261,737, Apr. 14, 1981.
3. Cullen, G. V., D. MacDonald, G. M. Pearson, and N. G. Siviour (assigned to University of Melbourne, Parkville, Victoria, Australia, Conzinc Riotinto of Australia Ltd. and Electrolytic Zinc Co. of Australasia Ltd., Melbourne, Victoria, Australia). Extraction of Metals From Solution by Metal-Loaded Brown Coal. Can. Pat. 981,593, Jan. 13, 1976.
4. Cullen, G. V., N. G. Siviour, and G. M. Pearson. Extracting Metals From Ammoniacal Solution With Low Rank Coals. *Metall. Trans. B*, v. 9B, Sept. 1978, pp. 409-413.
5. Fornwalt, H. J., and R. A. Hutchins. Purifying Liquids With Activated Carbon. *Chem. Eng.*, v. 73, No. 8, Apr. 11, 1966, pp. 179-184.



6. Fornwalt, H. J., and R. A. Hutchins. Purifying Liquids With Activated Carbon. *Chem. Eng.*, v. 73, No. 10, May 9, 1966, pp. 155-160.
7. Hatch, W. R. Removal of Cobalt From Ammoniacal Process Leach Solutions by a Conversion-Ion Exchange Process. Paper in Proceedings of the Eleventh Commonwealth Mining and Metallurgical Congress, Hong Kong, May 1978. *Inst. Min. and Metall.*, London, 1979, pp. 655-659.
8. Hurst, F. J. Separation of Cobalt From Nickel in Ammonia-Ammonium Carbonate Solutions Using Pressurized Ion Exchange. *Hydrometallurgy*, v. 1, 1976, pp. 319-338.
9. Inczedy, J. *Ioncserelek Analitika Alkalmazása* (Analytical Applications of Ion Exchangers). Pergamon, 1966, 443 pp.
10. Meites, L. *Handbook of Analytical Chemistry*. McGraw-Hill, 1963, 1781 pp.
11. Nakahara, S., and S. Mahajan. The Influence of Solution pH on Microstructure of Electrodeposited Cobalt. *J. Electrochem. Soc.*, v. 127, No. 2, 1980, pp. 283-288.
12. Nilsen, D. N., R. E. Siemens, and S. C. Rhoads. Solvent Extraction of Cobalt From Laterite-Ammoniacal Leach Liquors. BuMines RI 8419, 1980, 23 pp.
13. \_\_\_\_\_. Solvent Extraction of Nickel and Copper From Laterite-Ammoniacal Leach Liquors. BuMines RI 8605, 1982, 29 pp.
14. Nokin, J. Influence de Certains Facteurs sur la Précipitation Electrolytique du Cobalt (Influence of Certain Factors on the Electrolytic Precipitation of Cobalt). *Rev. Univers. Mines, Metall., Mec.*, v. 13, No. 6, 1957, pp. 220-232.
15. Paulson, L. E., and W. W. Fowkes. Changes in Ash Composition of North Dakota Lignite Treated by Ion Exchange. BuMines RI 7176, 1968, 18 pp.
16. Penner, L. R., D. E. Traut, and J. L. Henry. Neodecanoic Acid as a Cobalt<sup>3+</sup> Solvent Extractant. BuMines RI 8826, 1983, 10 pp.
17. Phillips, T. A. Private communication, 1982; available upon request from G. S. Slavens, Bureau of Mines, Albany, OR.
18. Rhoads, S. C., D. N. Nilsen, and R. E. Siemens. Solvent Extraction of Nickel, Cobalt and Copper From Laterite-Ammoniacal Leach Liquors. Paper in Proceedings International Solvent Extraction Conference (Toronto, Canada, Sept. 9-16, 1977). CIM, Montreal, Canada, v. 2, 1979, pp. 446-452.
19. Saha, A. K., M. J. Shahani, and V. A. Altekar. Adsorption of Cobalt by Lignite. *Hydrometallurgy*, v. 2, 1977, pp. 285-292.
20. Seitz, D. S., F. L. Minnear, and R. E. Dunbar. Ion Exchange Resins From Lignite Coal. *Ind. and Eng. Chem.*, v. 52, No. 4, 1960, pp. 313-314.
21. Siemens, R. E., and J. D. Corrick. Process for Recovery of Nickel, Cobalt and Copper From Domestic Laterites. *Min. Cong. J.*, v. 63, Jan. 1977, pp. 29-34.
22. Siemens, R. E., and P. C. Good (assigned to U.S. Dept. Interior). Process for Recovery of Non-Ferrous Metals From Oxide Ores and Concentrates. U.S. Pat. 3,929,468, Dec. 30, 1975.
23. Siemens, R. E., P. C. Good, and W. A. Stickney. Recovery of Nickel and Cobalt From Low-Grade Domestic Laterites. BuMines RI 8027, 1975, 14 pp.
24. Wang, F. T. The Sorptive Property of Coal. Paper in Proceedings of the 5th Underground Coal Conversion Symposium (Alexandria, VA, June 18-21, 1979). U.S. Dep. Energy, 1979, pp. 403-408; NTIS, CONF-790630.